



## Project Summary

# Reduction of Disinfection By-Product Precursors by Nanofiltration

J.S. Taylor, C.R. Reiss, P.S. Jones, K.E. Morris, T.L. Lyn, D.K. Smith, L.A. Mulford, and S. J. Duranceau

This document summarizes a project that investigated the cost and performance of employing a membrane process to remove disinfection by-product (DBP) precursors at highly organic groundwater and surface water sites. The groundwater investigation was followed by the surface water investigation. The main phases of the project at the groundwater and surface water sites were site selection, membrane selection, pretreatment studies and pilot plant operation for 1 yr at each site. Eleven different membranes were investigated at the groundwater site, Daytona Beach, FL, using a 1000 gpd membrane pilot plant to produce flow, pressure, and water quality samples. Nine membranes with molecular weight cutoff below 300 produced less than 0.10 mg/L DBP formation potential (FP) as  $\text{Cl}^-$  in the permeate. Only membranes classified as ultrafilters did not achieve DBPFP reduction of more than 90%. The pretreatment study at the groundwater site clearly demonstrated that only scaling control and prefiltration were required to control nanofilter fouling. A three stage 50,000 gpd pilot plant was operated for 8650 of 8704 hr available for production, experiencing less than 1% downtime. Average DBPFP in the permeate stream was 20  $\mu\text{g/L}$  as  $\text{Cl}^-$  and was more than 96% rejection of DBP precursors in the raw water. The average rate of mass transfer coefficient (MTC) decline during operation at the groundwater site was taken as  $2.2\text{E-}7/\text{d}^2$ , which did not include a period when new wells were placed on line before adequate flush-

ing was achieved. DBPFP in the permeate was independent of variation in pressure and recovery. The surface water site nanofiltration (NF) project was conducted at Melbourne, FL. Nine different membranes were tested for long-term operation using the same technique as used at the groundwater site. Seven of the tested membranes with molecular weight cutoffs of 300 removed 95% of the DBPFPs to less than 100  $\mu\text{g/L}$  as  $\text{Cl}^-$ . Membranes selected for long-term operation were the DuPont A15s\* (A15s) and the Desal DS5 (DS5) on the basis of precursor rejection and high productivity. Pretreatment studies demonstrated that conventional pretreatment alone or with sand filtration was not adequate to remove foulants at the surface water site. Alum coagulation-settling and rapid sand filtration (ACSSF), microfiltration (MF), and granular activated carbon (GAC) filtration were found to significantly reduce fouling in the pretreatment studies and were used in the pilot plant studies. Six different NF systems were studied at the surface water site consisting of three different pretreatments and two different membranes. These systems were operated for 16,770.8 out of 17,944.5 hr with less than 7% downtime. The AC-DS5 system was found to have the lowest rate of MTC decline,  $0.00010/\text{d}^2$ . GAC pretreatment was the least effective means of reducing MTC decline. Alum coagulation

\* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.



(AC), and the DS5 nanofilter were the most effective pretreatment process and membrane for minimizing MTC decline. The DBPFP averaged 22 µg/L as Cl<sup>-</sup> in the permeate stream and represented more than 98% reduction of the raw water DBPFP. Cost estimates for a 10 mgd groundwater NF plant were \$18,424,250 to construct and \$0.58/Kgal for operation and maintenance costs. Cost estimates for the 10 mgd surface water NF plants using alum, MF, and GAC pretreatment were \$26,402,250, \$30,537,250, and \$24,571,750 to construct and \$1.41/Kgal, \$0.96/Kgal, and \$1.04/Kgal for operation and maintenance costs, respectively.

*This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Analytical and Field Procedures

Standard analytical procedures as referenced in the 17<sup>th</sup> Edition of Standard Methods (SM) and EPA were utilized for this project with the exception of DBP, which were measured by interim EPA methods 551 for the base neutral and 552 for the acid extractable DBPs. The trihalomethanes (THMs) were measured by the approved EPA method 501 and were also measured as a base neutral in EPA method 551. Both 501 and 551 THMs are contained in the final report. THMs discussed in this document were measured using EPA method 551. Comparison of permeate THMs measured by EPA methods 501 and 551 found statistically equivalent measurements for total THMs, dichlorobromomethane and dibromochloromethane, but different for chloroform and bromoform. All methods and instruments were standardized and calibrated before use.

Field procedures included the installation and operation of a membrane pilot plant at the Daytona Beach, FL, groundwater site, and the installation and operation of three membrane pilot plants at the Melbourne, FL, surface water site. Field samples were transported to University of Central Florida (UCF) in ice filled coolers on the day of collection. Laboratory analysis of field samples was completed within the specified SM or EPA holding times which never exceeded 2 wk.

### Groundwater Study

The groundwater NF study for DBPFP reduction was divided into phases for membrane selection, pretreatment, and

long-term productivity. The groundwater site selected for the year of operation was located at the Daytona Beach Brennen water treatment plant on the east coast of Florida. This site was selected because of the high DBPFP, utility support, and proximity to UCF.

### Groundwater Membrane Selection

Eleven membranes were tested at Daytona Beach for DBP control and productivity with the use of a small-scale membrane unit. Nine of the 11 membranes tested met a 0.1 mg/L as Cl<sup>-</sup> DBP concentration limit, and from these, the A15s was selected on the basis of productivity. The A15s had an MTC of 0.0094 day<sup>-1</sup>.

### Groundwater Pretreatment Studies

A pretreatment study was performed using the bench-scale membrane system and one A15s membrane. The raw water was adjusted to pH 6.2 and continuously passed through a 5m filter for 571 hr at 30 to 65 psi and 20% to 25% recovery. The stability of the MTC demonstrated that no pretreatment other than acidification and filtration was required. Consequently only conventional membrane pretreatment was required for pilot plant operation at the groundwater site.

### Groundwater Operation

The plant personnel recorded pressure and flow daily and university personnel conducted trailer repairs, chemical makeup, and sample collections. The flow diagram of the groundwater site NF pilot plant is shown in Figure 1. Each pressure vessel contained three 4-in. x 40-in. membrane elements in series. During the year of operation, 8938.4 hr were available for operation. The pilot plant operated 8650 hr with 54 hr of unavoidable downtime and produced water more than 99% of the time.

A change in either pressure or recovery defined operational periods that are designated by number and vertical line in Figure 2, the system water MTC versus time. System recovery was varied from 70% to 90%, and feed pressure varied from 110 to 170 psi. In this figure three natural operational time periods were established by the MTC slope. The rate of MTC decline during the first period, from 0 to 4750 hr, was 6.53E-6/d<sup>2</sup>. This decline rate was representative of normal membrane fouling and deterioration. From 4750 to 5750 hr, the MTC declined at a rate of 3.96E-4/d<sup>2</sup>. During this time, new undeveloped wells were put on-line and caused increased colloidal fouling. The mem-

branes were cleaned with a high phosphate cleaner at hr 5750, and the MTC decline rate was 4.08E-6/d<sup>2</sup> for the remaining operation to 8650 hr. The MTC did not change as operating conditions changed but did decline steadily during operation. The overall MTC decline during the year of operation was 24%, 15% was attributed to normal membrane deterioration and 9% was attribute to irreversible well field fouling.

The raw, feed, and permeate DBPFP for the surface water and groundwater sites are reported in Table 1. Average DBPFP concentrations in the groundwater feed and system permeate were 503 and 20 µg/L as Cl<sup>-</sup>, respectively. THMs accounted for 72% and 75% of the feed and permeate DBPFP. The other major DBPs found in the feed water were haloacetic acids (HA), averaging 105 µg/L as Cl<sup>-</sup>, and chloral hydrate, averaging 32 µg/L as Cl<sup>-</sup>. The same DBPs, THMs, HA, and chloral hydrate found in the feed water were dominant in the system permeate. THM, FP, HA, and chloral hydrate averaged, 15, 3, and 2 µg/L as Cl<sup>-</sup> in the system permeate. Chloroform was the dominant species in the feed and system permeate, comprising 67% of the feed and 40% of the permeate DBPFP. The two major HA in the feed were di- and trichloroacetic acid, comprising 9% and 12% of the DBPFP. Mono-, di-, and trichloroacetic acid were the major HA in the permeate accounting for 5% each of the DBPFP. Over the year, 96% of the feed stream DBPFP was rejected and the permeate stream DBPFP never exceeded 0.1 mg/L as Cl<sup>-</sup>.

The total organic halogen formation potential (TOXFP) and non-purgable dissolved organic carbon (NPDOC), and selected inorganic water quality parameters for the surface and groundwater sites are reported in Table 2. On average, 96% of the TOXFP was rejected, corresponding to the rejection of DBPFP. NPDOC average rejection was 98%. Changing operating conditions of feed pressure and system recovery did not appear to affect the rejection of either TOXFP, NPDOC, or DBPFP. This result would indicate that the large organic molecules that comprise these groups are rejected by sieving rather than by diffusion. Calcium hardness averaged 264 mg/L as CaCO<sub>3</sub> in the feed and 22 mg/L as CaCO<sub>3</sub> system permeate. TDS averaged 368 mg/L in the feed and 48 mg/L in the system permeate.

### Surface Water Study

The surface water investigation was similar to the groundwater NF investigation in that a membrane selection, pretreatment, and long-term productivity stud-

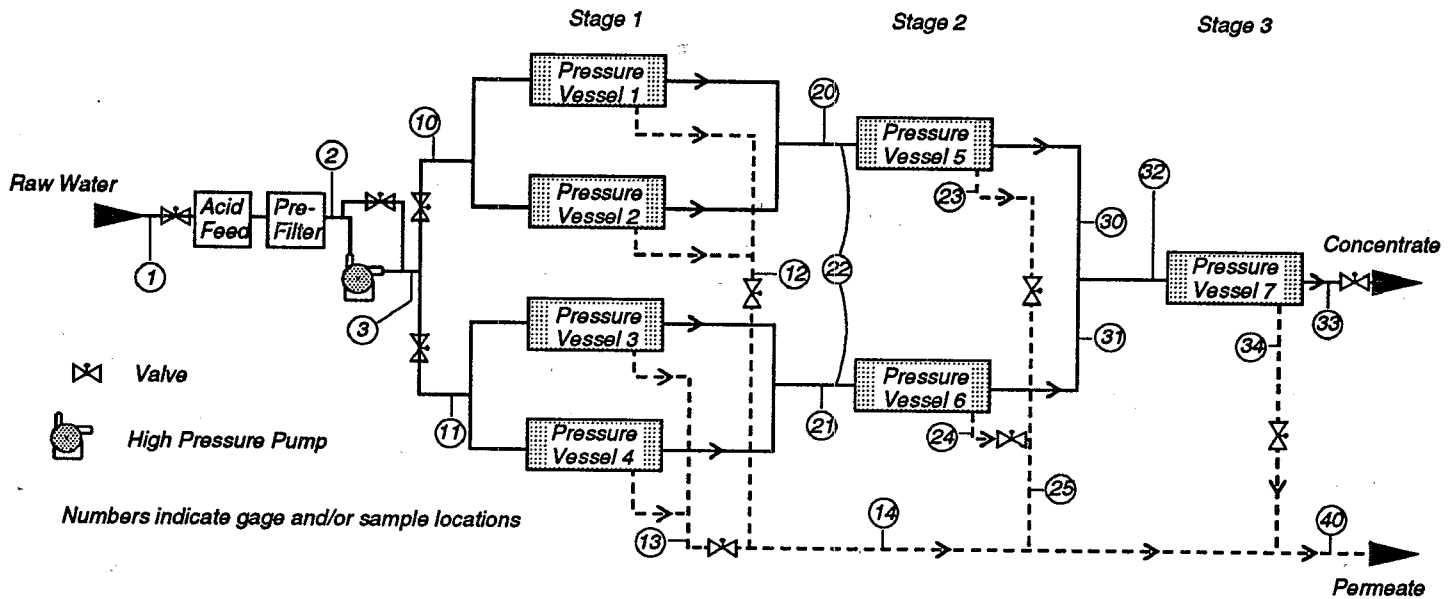


Figure 1. Groundwater membrane pilot plant flow diagram.

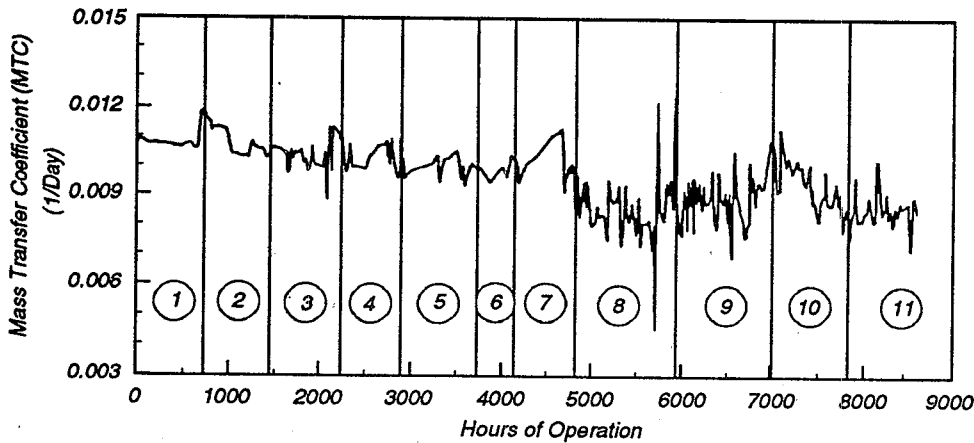


Figure 2. Groundwater system (MTC) for the nanofiltration pilot plant.

ies were conducted. After several potential surface water sites were considered for pilot plant operation, Melbourne, FL, was selected because of the very high FP of the water, city support, and the proximity to the university.

### Surface Water Site Membrane Selection

A total of 10 different spiral-wound thin-film composite membranes were investigated for pilot plant operation by monitoring flow and pressure and by analyzing water quality samples collected during the operation of each of the membranes in a single element system. Seven of the

tested membranes reportedly have molecular weight cutoffs less than 300 and removed more than 95% of the DBPFP from 1522  $\mu\text{g/L}$  to less than 100  $\mu\text{g/L}$  as  $\text{Cl}^-$ . The productivity of the membranes as measured by the water MTC ranged from 0.0041/d to 0.0296/d averaging 0.0094/d. Two membranes, an A15s and a DS5, were selected on the basis of DBPFP precursor rejection and high productivity.

### Surface Water Site Pretreatment Studies

Four different pretreatment techniques in addition to conventional pretreatment

for a NF membrane process were investigated on a short-term basis. Each of the four techniques included conventional pretreatment, which is typically defined as prefiltration through a filter with pore diameters of 5 to 20m and acid or antiscalant addition to keep a salt from precipitating on the feed stream side of the membranes. The pretreatment techniques were conventional pretreatment, sand filtration, ACSSF, MF, and GAC filtration. The effectiveness of the pretreatment techniques was judged by the resulting MTC decline over time of operation. Limiting the MTC decline to a maximum of 15% over an assumed 2-wk operation period results in an MTC decline rate 0.0001/d<sup>2</sup> for a typical nanofilter.

The conventional pretreatment system, 5m prefiltration and scaling control, resulted in less than 2 hr of operation before the prefilter had to be replaced. Sand filtration in addition to conventional pretreatment resulted in less than 8 hr of operation before the prefilter had to be replaced. These experiments clearly demonstrated that conventional pretreatment and sand filtration in addition to conventional pretreatment using a disburstant was not adequate for fouling control at the surface water site.

The remaining pretreatment systems (ACSSF, MF, and GAC) were more effective. ACSSF pretreatment resulted in an MTC decline rate of 0.00035/d<sup>2</sup> during runtimes varying from 40 to 70 hr. A Memcor cross-flow microfilter (CFMF) was

**Table 1. Organic Water Quality Summary ( $\mu\text{g/L}$  as  $\text{Cl}^-$ ) for Groundwater and Surface Water Site Nanofiltration Pilot Plant Site**

|                             | Raw Water Source |         | Surface Feed |      |      | Ground |         |          |         | Surface |          |          |          |
|-----------------------------|------------------|---------|--------------|------|------|--------|---------|----------|---------|---------|----------|----------|----------|
|                             | Ground           | Surface | AC           | MF   | GAC  | PERM   | PERM    | PERM     | PERM    | PERM    | PERM     | PERM     | PERM     |
|                             |                  |         |              |      |      | A158   | AC-A15s | CGMG-DS5 | GAC-DS5 | AC-DS5  | DFMF-DS5 | GAC-A15s | GAC-A15s |
| NPDOC (mg/L)                | 9                | 29      | 10           | 27   | 23   | 0.2    | 0.1     | 0.2      | 0.1     | 0.4     | 1.6      | BDL      | 1.3      |
| TOXFP                       | 1120             | 6232    | 1248         | 4925 | 3467 | 43     | 56      | 47       | 94      | 74      | 56       | 62       | 45       |
| DBPFP                       | 503              | 2446    | 478          | 1939 | 1342 | 20     | 18      | 30       | 14      | 35      | 26       | 16       | 18       |
| Bromochloroacetonitrile     | 0                | 4       | 3            | 3    | 3    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Dichloroacetonitrile        | 2                | 27      | 4            | 35   | 3    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Dibromoacetonitrile         | 0                | 1       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Trichloroacetonitrile       | 0                | 1       | 0            | 1    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Carbon tetrachloride        | 0                | 1       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Trichloroethylene           | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Tetrachloroethylene         | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| 1,1,1-Trichloroethane       | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 1        | 0        | 0        |
| 1,2-Dibromoethane           | 0                | 0       | 1            | 0    | 0    | 0      | 0       | 1        | 0       | 0       | 0        | 0        | 0        |
| 1,2-Dibromo-3-chloropropane | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Chloroform                  | 335              | 865     | 176          | 735  | 502  | 8      | 3       | 3        | 1       | 4       | 1        | 1        | 2        |
| Bromodichloromethane        | 27               | 80      | 65           | 84   | 68   | 5      | 4       | 8        | 3       | 7       | 4        | 2        | 3        |
| Chlorodibromomethane        | 1                | 5       | 20           | 5    | 5    | 2      | 4       | 7        | 3       | 10      | 7        | 5        | 5        |
| Bromoform                   | 0                | 3       | 3            | 0    | 0    | 0      | 1       | 3        | 3       | 6       | 5        | 3        | 2        |
| 1,1-Dichloropropanone       | 0                | 2       | 0            | 3    | 3    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| 1,1,1-Trichloropropanone    | 1                | 43      | 13           | 40   | 26   | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Chloropicrin                | 0                | 1       | 3            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| Chloral hydrate             | 32               | 187     | 40           | 146  | 62   | 2      | 0       | 2        | 0       | 1       | 1        | 0        | 1        |
| Monochloroacetic acid       | 2                | 9       | 4            | 8    | 6    | 1      | 1       | 1        | 0       | 2       | 4        | 0        | 1        |
| Monobromoacetic acid        | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 1        | 1        |
| Dichloroacetic acid         | 43               | 336     | 60           | 267  | 182  | 1      | 2       | 1        | 1       | 2       | 1        | 2        | 1        |
| Dibromoacetic acid          | 0                | 2       | 3            | 2    | 3    | 0      | 2       | 3        | 1       | 2       | 2        | 1        | 2        |
| Trichloroacetic acid        | 60               | 878     | 80           | 630  | 452  | 1      | 1       | 1        | 0       | 1       | 0        | 1        | 0        |
| 2-Chlorophenol              | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| 2,4-Dichlorophenol          | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |
| 2,4,6-Trichlorophenol       | 0                | 0       | 0            | 0    | 0    | 0      | 0       | 0        | 0       | 0       | 0        | 0        | 0        |

used to pretreat the raw water before NF. Operational times up to 365 hr using only the CFMF were achieved before CFMF fouling terminated the experiment. CFMF-NF series operation achieved run times of 110 to 150 hr before a scheduled termination was implemented. The NF MTC decline rate was  $0.0006/\text{d}^2$  to  $0.0008/\text{d}^2$  in these studies. The CFMF flux was varied from 70 to 161  $\text{gal}/\text{ft}^2/\text{day}$  (gsfd). CFMF fluxes less than 100 gsfd resulted in longer times of operation. GAC pretreatment resulted in NF MTC declines of  $0.0010/\text{d}^2$  or higher. The longest time of operation (approximately 40 to 60 hr) was achieved at the lowest GAC surface loading rates (SLR). GAC SLRs were varied from 1.54 to 0.72  $\text{gal}/\text{ft}^2/\text{min}$ .

The surface water site pretreatment studies demonstrated that some form of pretreatment would significantly decrease the rate of NF MTC decline and cleaning frequencies. All pretreatment processes had reduced NF fouling relative to conventional pretreatment. CFMF was the most effective process for reducing the rate of MTC decline, but the results of the pretreatment study showed ACSSF and

GAC as effective processes for reduction of NF fouling. The pilot plant was modified from a three-stage system to two separate two-stage systems. The CFMF was used in series with the single-stage pilot plant, and the modified pilot plant was used to investigate GAC and alum coagulation pretreatment. Consequently all pretreatment processes were evaluated in long-term operation at the surface water site.

### Surface Water Site Operation

Six separate systems were evaluated on a long-term basis at the surface water site that involved three different pretreatment processes and two different nanofilters. The pretreatment systems — ACSSF, GAC, and both crossflow and direct flow microfiltration (CFMF, DFMF) — were used in advance of the DS5 and the A15s nanofilters. The systems are abbreviated as AC-A15s, CFMF-DS5, GAC-DS5, AC-DS5, DFMF-DS5, and GAC-A15s. A single-stage NF system was used to pilot the CFMF-DS5 and the DFMF-DS5 systems. The remaining NF systems were operated using a two-stage

pilot plant. The AC-A15s, GAC-DS5, and CFMF-DS5 systems were operated simultaneously in the initial phase of the project. The AC-DS5, GAC-A15s, and DFMF-DS5 were operated simultaneously in the latter phase of the project.

### Run Time Analysis

The six NF systems were available for operation a total of 20,141.3 hr and experienced a total downtime of 3373.5 hr, which was subdivided into avoidable and unavoidable downtime. Avoidable downtime was classified as time generated due to research preparation. Unavoidable downtime, lost because of normal production activities, totaled 1173.7 hr. The unavoidable downtime, which varied from 5% to 10%, averaged 7% of the production time taken as the sum of the runtime and the unavoidable downtime. Two of the major categories of unavoidable downtime were power interruption due to main plant shutdown and filter backwash, which accounted for 23% and 10% of the unavoidable downtime and would be avoided in an actual membrane plant environment. The surface water site NF systems con-

**Table 2. Inorganic Water Quality Summary for Groundwater and Surface Water Site Nanofiltration Pilot Plant Sites**

| Parameter               | Units                        | Raw Water Source |         | Surface Feed |      |      | Ground    | Surface      |               |              |             |               |               |               |
|-------------------------|------------------------------|------------------|---------|--------------|------|------|-----------|--------------|---------------|--------------|-------------|---------------|---------------|---------------|
|                         |                              | Ground           | Surface | AC           | MF   | GAC  | PERM A15s | PERM AC-A15s | PERM CFMF-DS5 | PERM GAC-DS5 | PERM AC-DS5 | PERM DFMF-DS5 | PERM GAC-A15s | PERM GAC-A15s |
| Color                   | (CPU)                        | 31               | 224     | 12           | 167  | 149  | 1         | 1            | 1             | 0            | 1           | 1             | 0             | 1             |
| TDS                     | (mg/L)                       | 368              | 379     | 458          | 364  | 358  | 48        | 38           | 228           | 169          | 162         | 230           | 149           | 119           |
| Sodium                  | (mg/L)                       | 20               | 46      | 47           | 45   | 39   | 7         | 15           | 32            | 29           | 36          | 37            | 28            | 20            |
| Total Hardness          | (mg/L as CaCO <sub>3</sub> ) | 289              | 138     | 196          | 141  | 135  | 25        | 26           | 56            | 49           | 27          | 65            | 43            | 26            |
| Calcium Hardness        | (mg/L as CaCO <sub>3</sub> ) | 264              | 99      | 148          | 101  | 101  | 22        | 23           | 53            | 37           | 18          | 45            | 26            | 18            |
| Chloride                | (mg/L)                       | 29               | 93      | 98           | 94   | 87   | 5         | 34           | 85            | 68           | 77          | 84            | 51            | 40            |
| Sulfates                | (mg/L)                       | 0.3              | 0       | 90           | 0    | 4    | 2         | 6            | 1             | 29           | 16          | 0             | 0             | 0             |
| Alkalinity              | (mg/L)                       | 295              | 95      | 65           | 111  | 82   | 22        | 4            | 88            | 25           | 0           | 29            | 24            | 8             |
| pH                      | 6.3                          | 7.7              | 7.3     | 7.8          | 7.5  | 4.4  | 3.7       | 6.5          | 3.2           | 2.9          | 4.8         | 6.4           | 5.6           |               |
| Iron                    | (mg/L)                       | 374              | 304     | 71           | 154  | 165  | 32        | 11           | 3             | 4            | 35          | 25            | 120           | 2             |
| Turbidity               | (NTU)                        | 0.67             | 5.33    | 0.42         | 0.16 | 0.93 | 0.14      | 0.11         | 0.12          | 0.02         | 0.00        | 0.04          | 0.20          | 0.04          |
| Heterotopic Plate Count | (CFU/mL)                     | 63               | 3174    | 1427         | 978  | 2030 | 410       | 409          | 351           | 173          | 146         | 1129          | 1123          | 1000          |

sistently produced water on average more than 93% of the time.

### System Water Quality

The organic solute average concentrations for the most frequently observed DBPFPs from different systems were analyzed statistically. The analysis indicated that systems involving DFMF pretreatment and the AC-DS5 system produced statistically different average permeate concentrations. These occurrences were most common to the THM and HA species; when the occurrences were compared with the average DBPFPs of each system, the AC-DS5 system and systems involving DFMF pretreatment were found to be the least effective for DBP precursor removal.

Percent NPDOC removal through only the nanofilter for the corresponding system percent recovery and pressure gradient, as shown in Figure 3 for the CFMF-DS5 system, is independent of the operating conditions or percent recovery. This same trend was found for all systems. In a diffusion controlled process, the solute percent removal would increase as pressure increase and recovery decreased. That trend may be slightly evident for the AC-DS5 and GAC-DS5 systems, but the opposite or, more likely, no trend was indicated for the remaining systems. Sieving is indicated as the major mechanism of NPDOC removal because the percent of NPDOC removal is largely unaffected by variations in pressure and recovery. As NPDOC is representative of DBPFP precursors, the majority of DBPFP reduc-

tion would be realized by sieving and would be independent of process optimization at high flux and low recovery. A similar relationship for general DBPFP and TOXFP independence from pressure and recovery was also observed. Consequently these data indicate that a very high DBPFP reduction may be realized by NF but that optimization of a given membrane for DBPFP reduction is not feasible by varying pressure and recovery. The data in Table 1 show that the permeate DBPFP varied from 14 to 35 µg/L as Cl<sup>-</sup> and averaged 22 µg/L as Cl<sup>-</sup> for all systems. The two lowest permeate DBPFP average concentrations were realized by the GAC-DS5 and the GAC-A15s two-stage systems. The highest DBPFP average concentration was realized by the AC-DS5 system. These results indicated that a THM concentration below 50 µg/L, but not below 25 µg/L, as the species could be consistently maintained in a field application. The ratio of DBPFP, THMFP, and HAFP to TOXFP was statistically equivalent in the raw, feed, and permeate streams for each system at all sites. The ratio of brominated species was greater in the permeate than in the feed or raw streams at the surface water site for all systems. The concentrations of chlorodibromomethane, bromoform, and dibromohaloacetic acid was in general greater or equal in the permeate stream as opposed to the raw and feed streams. The THMFP of the AC-A15s, GAC-DS5, and GAC-A15s systems was 11 or 12 µg/L as Cl<sup>-</sup> and was the lowest for the six

systems. The AC-DS5 system recorded the highest THMFP, 27 µg/L as Cl<sup>-</sup>. The HA concentration in the permeate from the six systems ranged from 2 to 7 µg/L as Cl<sup>-</sup> with dibromoacetic acid being the most prevalent.

The inorganic species was dependent on NF pressure and recovery, which is indicative of a diffusion controlled solute mass transfer process. Consequently inorganic permeate concentration varied by changing pressure and recovery but organic permeate concentration did not in these studies. All NF systems effectively reduced color to 0 or 1 cpu on average. The calcium hardness ranged from 18 to 53 mg/L as CaCO<sub>3</sub>. All systems realized moderate sodium removal. The AC-A15s system achieved the lowest sodium concentration in the permeate stream, 15 mg/L. The microfilter was the most effective pretreatment process for removal of turbidity and heterotrophic plate count reduction.

### System Productivity

The NF pilot plants were operated in time intervals or periods specified by different combinations of flux and recovery. Four operating conditions were used to evaluate the performance of the 2-stage pilot plant using GAC or alum coagulation pretreatment: 10 gsf/d/45%, 10 gsf/d/65%, 15 gsf/d/45%, and 15 gsf/d/65%. Six different operating conditions were used to evaluate the performance of the single-stage pilot plant, which specified nanofilter flux, nanofilter recovery, and microfilter flux:

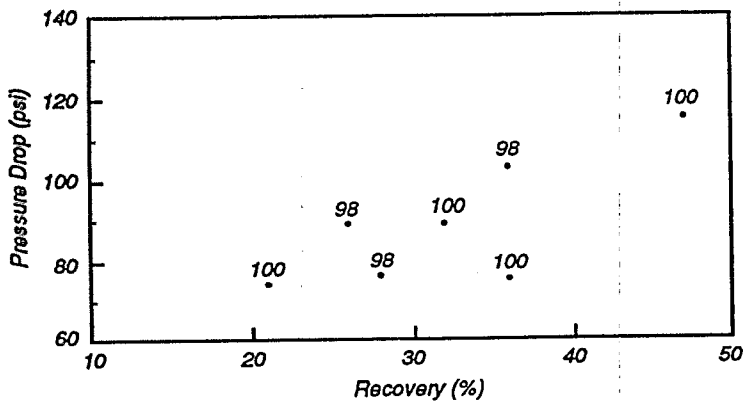


Figure 3. Percent NPDOC rejection for the CFMF-DS5 surface water site nanofiltration system.

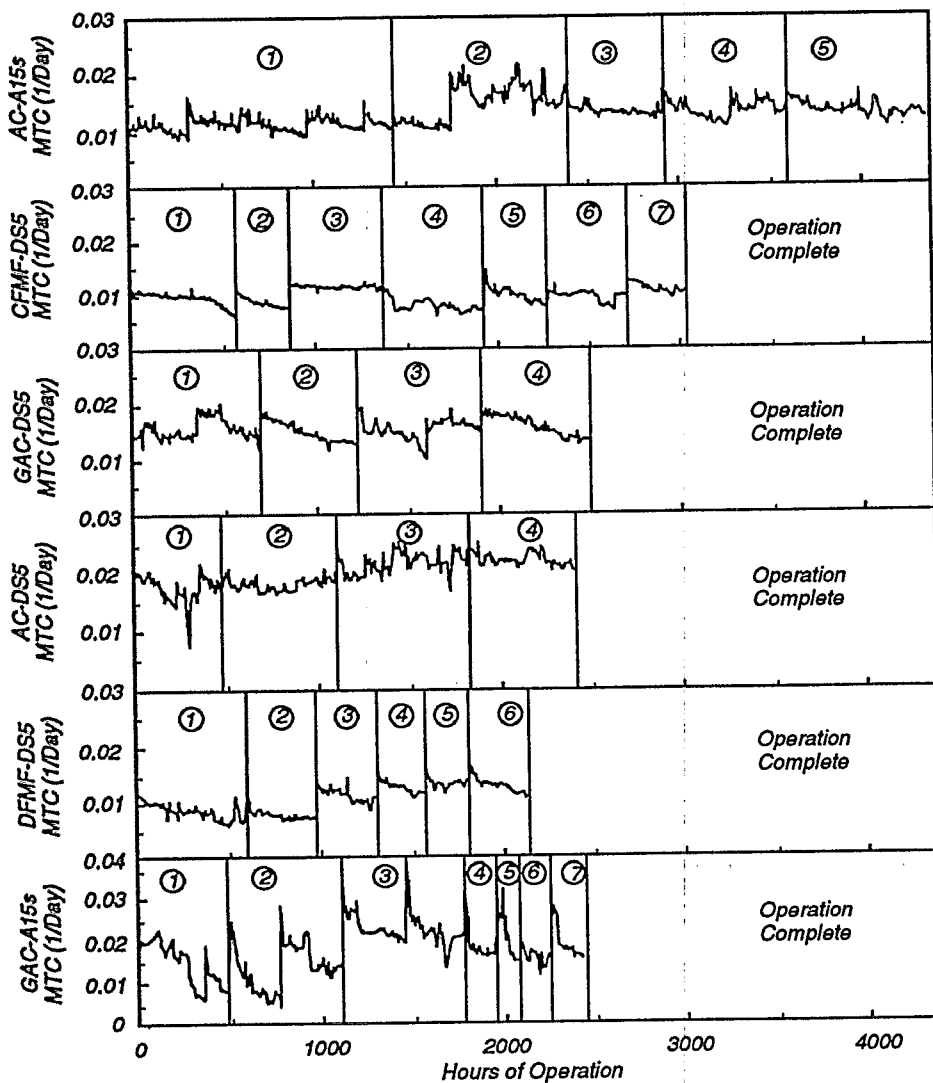


Figure 4. Mass transfer coefficients for the various pretreatment systems for the surface water nanofiltration site.

10gsfd/15% and 15 gsfd/24% each in combination with 50 gsfd, 75 gsfd, and 100 gsfd. The GAC-A15s system was also operated as a single-stage system so that a lower GAC SLR could be evaluated. The MTC declined with time within periods of operation and is shown in Figure 4 for all the surface water site NF systems. The abrupt changes occurred when the nanofilters were cleaned.

The productivity of each of the six surface water site NF systems was analyzed by determining the change of the MTC (1) with respect to time of operation by linear regression and (2) with respect to time of operation, surficial membrane velocity, membrane flux, feed stream NPDOC concentration, and microfilter flux by multivariate linear regression. The multivariate linear regression equation is shown below:

$$MTC = A + B(FR) + CT + DF + EO + G(MF)$$

where: MTC = mass transfer coefficient, 1/d  
 A = constant  
 B, C, D, E, G = linear regression coefficients  
 $FR = (F/2)(1/R + (1-R/R))$ , gsfd  
 T = time of operation, hr  
 O = NPDOC, mg/L  
 F = nanofilter flux, gsfd  
 MF = microfilter flux, gsfd  
 R = decimal fraction NF recovery

The results of this analysis are shown in Table 3. Only the time and MF coefficients have a consistent sign, negative. This would indicate a changing relationship between fouling and the remaining variables identified in the regression equation. The lack of a consistent sign on the FR, F, and NPDOC coefficients for the model will not support any readily apparent overall interpretation of horizontal flux, vertical flux, and NPDOC on water productivity. The system productivity did always decrease with time and MF flux. Both linear models were descriptive of the MTC with a high level of confidence, but a significant amount of the variation between the actual and predicted MTCs cannot be accounted for by the models.

Initially, during simultaneous operation, the CFMF-DS5 system had the least MTC decline with time, 3.99E-6, which was 36% less than the AC-A15s system and 255% less than the GAC-DS5 system. All NPDOC coefficients were negative during the initial operation as expected. The CFMF-DS5 system MTC was less effected by NPDOC than were the other systems. The CFMF-DS5 NPDOC coefficient was

-1.2E-4, which was approximately one-third of the GAC-DS5 and one-sixth of the AC-A15s NPDOC coefficients during this time period. Interestingly, the highest NPDOC concentrations were received by the CFMF-DS5 system, 25 mg/L, as compared with 20 mg/L for the GAC-DS5 system and 8 mg/L for the AC-15s system. The rate of MTC decline with respect to NF flux was unexpectedly positive varying from 1.46E-4 to 2.57E-4.

During the simultaneous operation in the latter phase of the project, the AC-DS5 system was found to have the least rate of MTC decline with time as shown by the multivariate regression coefficient for time, -5.26E-7, which was more than one order of magnitude less than that of the DFMF-DS (-7.77E-6) or that of the

GAC-A15s (-8.42E-6). The AC-DS5 system had the least rate of MTC decline with respect to time for both the linear and multivariate regression. The regression coefficients for FR, flux, and NPDOC varied positively and negatively during the latter simultaneous operation period; this does not indicate any apparent relationship to MTC and was unexpected.

The multivariate MTC analysis indicated that any surface water system using GAC pretreatment had the most rapid rate of MTC declines, which was approximately an order of magnitude more than other systems; the DS5 membrane was less fouled during operation; and the alum coagulation pretreatment produced the least rate of MTC decline. The GAC-A15s sys-

tem was operated as a single-stage system to determine if the rate of MTC decline could be lessened by a reduced GAC SLR; however, the rate of MTC decline increased as the GAC SLR decreased. These results demonstrated that the DS5 nanofilter was less fouling than the A15s nanofilter; that decreasing GAC SLR did not reduce nanofilter fouling; and that the indicated rate of nanofilter MTC decline by pretreatment was alum coagulation < MF < GAC. The linear regression of MTC with time indicated that GAC pretreatment was the least effective treatment for the reduction of fouling; that the AC-DS5 system experienced the least rate of MTC decline (0.000100/d<sup>2</sup>); that the DS5 membrane had a slightly better rate of MTC decline; and that alum coagulation was a better pretreatment process for fouling reduction.

**Table 3. Surface Water Site Solvent Mass Transfer Coefficient (MTC) Multiple Regression**

| System       | Constant | Coefficients    |                 |                 |                 |                 | R <sup>2</sup> | F   | d(MTC)<br>dt |
|--------------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|-----|--------------|
|              |          | FR              | Time            | NF<br>Flux      | NPDOC           | MF              |                |     |              |
|              |          | 10 <sup>5</sup> | 10 <sup>5</sup> | 10 <sup>4</sup> | 10 <sup>4</sup> | 10 <sup>5</sup> |                |     |              |
| AC-A15s Old* | 0.013    | -4.27           | -0.70           | 2.02            | -2.41           |                 | 0.450          | 100 | -2.53        |
| AC-A15s New  | 0.021    | -16.6           | -0.54           | 2.45            | -7.47           |                 | 0.452          | 67  | -2.10        |
| CFMF-DS5     | 0.013    | 6.55            | -0.040          | 1.46            | -1.20           | -3.38           | 0.317          | 46  | -1.89        |
| GAC-DS5      | 0.025    | 25.7            | -1.02           | 2.57            | -3.39           |                 | 0.648          | 146 | -2.25        |
| AC-DS5       | 0.016    | 45.1            | -0.05           | -4.27           | 1.68            |                 | 0.475          | 58  | -1.00        |
| DFMF-DS5     | 0.014    | -1.43           | -0.78           | -1.12           | -1.77           | -7.12           | 0.668          | 96  | -1.88        |
| GAC-A15s**   | -0.009   | 95.7            | -0.84           | 5.97            | 1.80            |                 | 0.610          | 76  | -6.02        |
| GAC-A15s*    | 0.002    | -35.6           | -3.93           | 9.96            | 8.47            |                 | 0.662          | 31  | -17.4        |

\* Used at Groundwater Site

\*\* Single Stage

**Table 4. Summary Cost Table for Various Water Treatment Processes for a 10 MGD Membrane Nanofiltration Plant**

| Type of plant |          | Advanced Pretreatment | Membrane       | Total Cost \$/Kgal |
|---------------|----------|-----------------------|----------------|--------------------|
| Groundwater   | Capital: | None                  | Nanofiltration |                    |
|               | \$       | 0                     | 18,424,250     |                    |
|               | \$/Kgal  | 0                     | 0.59           |                    |
|               | O & M    | 0                     | 2,109,000      |                    |
|               | \$/Kgal  | 0                     | 0.58           | 1.17               |
| Surface water | Capital: | Alum                  | Nanofiltration |                    |
|               | \$       | 5,494,000             | 20,908,250     |                    |
|               | \$/Kgal  | 0.18                  | 0.67           |                    |
|               | O & M:   | 2,835,000             | 2,304,000      |                    |
|               | \$/Kgal  | 0.78                  | 0.63           | 2.26               |
| Surface water | Capital: | GAC                   | Nanofiltration |                    |
|               | \$       | 3,663,500             | 20,908,250     |                    |
|               | \$/Kgal  | 0.12                  | 0.67           |                    |
|               | O & M    | 760,400               | 3,054,000      |                    |
|               | \$/Kgal  | 0.20                  | 0.84           | 1.83               |
| Surface water | Capital: | Microfiltration       | Nanofiltration |                    |
|               | \$       | 9,980,000             | 20,557,250     |                    |
|               | \$/Kgal  | 0.32                  | 0.66           |                    |
|               | O & M    | 938,000               | 2,514,000      |                    |
|               | \$/Kgal  | 0.27                  | 0.69           | 1.94               |

### Cost Estimates

Cost estimates (Table 4) for the construction, operation, and maintenance of representative 10 mgd NF plants at groundwater and surface water sites were developed for an NF system that consisted of prefiltration, acid addition, NF, packed tower aeration, disinfection, stabilization, and storage. Additional pretreatment costs were incorporated in the surface water estimates: ACSSF, MF, and GAC filtration. All capital costs were amortized for 20 yr at 10%, and all unit costs (\$/Kgal) are based on 10 mgd of finished product water.

The groundwater cost estimate for the NF plant was based on 85% recovery and 15 gsf/d flux. The total cost estimate for constructing, operating, and maintaining an NF plant at the groundwater site was \$1.17/Kgal. Only conventional pretreatment (acid addition and prefiltration) is required. Construction cost was estimated at \$18,424,250 (\$0.59/Kgal); the O&M cost at \$2,109,000/yr (\$0.58/Kgal).

An NF system constructed and operated at Melbourne, utilizing a surface water source, would have a higher cost due to required pretreatment. The surface water NF plants were based on a 10 gsf/d flux and 75% recovery. The cost estimate to build and operate a 10 mgd GAC-NF system was \$24,571,750 or \$1.83/Kgal. The total cost estimate to build and operate a 10 mgd AC-NF system was \$26,402,250 or \$2.26/Kgal. The total cost estimate to build and operate a 10 mgd MF-NF system was \$30,537,250 or \$1.94/Kgal.

### Summary

NF pilot plants processing highly organic raw waters were operated at a

Daytona Beach, FL, groundwater site for 8650 hr and at a Melbourne, FL, surface water site for 16,770.8 hr. Both plants consistently removed 98% of the DBPFP, which averaged 20 and 22  $\mu\text{g/L}$  as  $\text{Cl}^-$ , respectively, in the finished water. The rate of MTC decline averaged approximately  $2\text{E-}7/\text{d}^2$  and  $2\text{E-}4/\text{d}^2$ , respectively, and the approximate cleaning frequency at the groundwater and surface water sites

was 6 mo and 1 wk, respectively. The order of the pretreatment processes based on the least rate of NF MTC decline was alum coagulation, MF, and GAC filtration. The removal of DBP precursors by NF was independent of pressure and recovery variations at both sites, which indicates DBP rejection by NF can be predicted by a sieving as opposed to a diffusion model. The cost estimate for the

groundwater plant was \$0.59/Kgal for construction and \$0.58/Kgal for operation. The least costly surface water plant used GAC pretreatment and was estimated to be \$0.79/Kgal for construction and \$1.04/Kgal for operation and maintenance.

The full report was submitted in fulfillment of CR 815288 by the University of Central Florida under the sponsorship of the U.S. Environmental Protection Agency.

*J.S. Taylor, C.R. Reiss, P.S. Jones, K.E. Morris, T.L. Lyn, D.K. Smith, L.A. Mulford, and S.J. Duranceau are with the University of Central Florida, Orlando, FL 32816.*

*J. Keith Carswell was the EPA Project Officer (see below).*

*The complete report, entitled "Reduction of Disinfection By-Product Precursors by Nanofiltration," (Order No. PB92-149 269/AS; Cost: \$73.00, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*For further information, Jeff Adams can be contacted at:*

*Risk Reduction Engineering Laboratory*

*U.S. Environmental Protection Agency*

*Cincinnati, OH 45268*

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati, OH 45268

BULK RATE  
POSTAGE & FEES PAID  
EPA  
PERMIT NO. G-35

Official Business  
Penalty for Private Use \$300

EPA/600/SR-92/023